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Particularly in regard to the
Influence of Copper
and Mill Scale



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— BY —

E. A. RICHARDSON
220 Floyd Street, Toledo, Ohio

AND

L. T. RICHARDSON
322 Twentieth Street, Milwaukee, Wis.

*A paper read before the Thirtieth General Meeting of the American Electro-chemical Society,
held in New York City, September 28-30, 1916.*

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The corrosion of iron and steel is a question that is becoming of increasingly great importance. The problem of finding the true nature of and the ultimate causes that underlie the rusting of iron is as yet unsolved. Much work has been done in the past, is being done at present and before the problem is solved, much more will undoubtedly be done in the future.

The paper will not burden itself with a lengthy review of previous work that has been done upon the subject, but will confine itself to a brief summary of such work.

As regards the relative merits of wrought iron and steel much work has been done, but observations on the two materials seem to be in poor agreement.

Of recent years the question of the rust-resisting properties of copper-bearing steels has arisen and remains as yet unsettled, the chief contenders being the makers of copper-bearing steel and those of pure iron. As far as numerical data are concerned, the advocates of copper-bearing steel seem to be in the lead; in fact it seems to the writers that one weakness in the argument of the pure iron advocates is that they give little numerical data to support their claims. To many, their arguments would carry much more weight if such data were included.

Briefly, up to about 1910, a considerable amount of work had been done upon the subject of copper in steel, but

this work was mainly in the form of fragmentary observations on steels that contained small quantities of copper either accidentally or intentionally added, and a few actual tests upon copper-bearing material. Previous to this time there appeared to be no acute controversy as to the effect of copper in steel upon corrosion, although judging from the literature it did exist at this time to a rather mild extent as to the effect of this metal upon the physical properties of steel. The general impression, one would gain from reading these articles, is that copper in steel is a benefit as regards resistance to corrosion.

Shortly after 1910 copper-bearing steel was put upon the market as a corrosion-resisting material. The controversy then became acute, the chief objectors being the advocates of pure iron. The result has been that a considerable amount of work has been done and published without settling the question. Most of this work seems to have been done by those interested in copper-bearing steel in their efforts to prove that this material is the real rust-resisting material they claim it to be. A large share of the published work, which contains results from tests closely approaching actual service conditions, has been done by Mr. D. M. Buck¹—a strong advocate of copper-bearing steel. The opposing side appears mostly in discuss-

¹ Buck, D. M. Copper in Steel—The Influence on Corrosion. *Jour. of Ind. and Eng. Chem.*, June, 1913.

Buck, D. M., and Handy, J. O. Research on the Corrosion Resistance of Copper Steel. *Jour. Ind. and Eng. Chem.*, March, 1916.

sion of these and other papers and appears to be taking a defensive stand. The impression, gained by the writers, from reading the available published evidence, is that copper-bearing steels do possess rust-resisting properties and are superior to any iron or steel now on the market.

Likewise, the influence of mill-scale upon the corrosion of iron is under discussion.

Friend² for instance states that "traces of oxides upon the surface of metals are powerful stimulators of corrosion."

A. Sang³ says, "Black oxide only protects provided it is continuous and firmly anchored to the iron (Bower-Barfing, etc.) ; as mill-scale, which is loose and fissured, it is detrimental, the iron in contact with it and exposed rusts about 50 percent faster."

Aston and Burgess⁴ find "that mill-scale had an accelerating effect for an atmospheric test and a retarding action for a fume test." Further they state that "there is no doubt that the protective property of mill-scale is dependent upon its physical properties, continuity, etc."

G. C. Whipple and M. C. Whipple⁵ tested steel, ingot iron and wrought iron with mill-scale and with mill-scale removed and obtained erratic results, but, generally speaking, the rusting was slightly greater in the case of the metals from which the mill-scale had been removed than in the cases of the metals on which the mill-scale had been left. They state, however, "that the best remedy to protect steel from pitting is to remove mill-scale."

Buck and Handy⁶ in their latest paper state "at the time of exposure of the full-sized corrugated sheets careful notes were taken concerning the physical appearance of the sheets as affected

by the amount of mill-scale which was present, and as to whether they were outside or inside in the pack. During the progress of the test this feature was carefully watched, and the time of ultimate failure of sheets whose surfaces were comparatively free from mill-scale was compared with others of the same grade, whose surfaces were well covered with mill-scale. From these observations, we concluded that the influence of this original surface oxide is slight, and is lost in the early stages of rusting, for no difference in final failure could be noticed."

One thing, however, in regard to many tests that have been made upon the relative corrosion of iron and steel, is that insofar as the ultimate consumer is concerned, they are not of the greatest value, since many times only two or three materials were compared, or the materials were made especially for test and cannot be obtained in commercial quantities. Such tests do not carry the most weight since they do not have the air of disinterestedness that exists in the case of materials purchased upon the open market. In fact one of the arguments of the pure iron advocates is the objection to "special tests" and the demand of basing comparisons upon service tests only.

In view of the fact that no results had been published of a complete test on commercial materials, it was deemed desirable to make a test containing all the types of iron and steel that could be obtained.

Some of the kinds of materials that are commonly used for structures, exposed to atmospheric corrosion, are:

1. Steel.
2. Puddled Iron.
3. Commercially Pure Iron.
4. Copper-Bearing Steel.
5. Cast Iron.

This paper deals with the first four classes.

Accordingly there were obtained upon the market the following materials in

² Friend, J. N. *The Corrosion of Iron and Steel*. p. 251.

³ Sang, A. *The Corrosion of Iron and Steel*. p. 81.

⁴ Aston, James, and Burgess, C. F. *The Rate of Rusting of Iron and Steel*. Eighth Int. Congress of Applied Chem., 26, 453.

⁵ Whipple, G. C., and Whipple, M. C. *Mill-Scale as a Cause of Corrosion*. Eighth Int. Congress of Applied Chem.

⁶ Buck, D. M., and Handy, J. O. *Research on the Corrosion Resistance of Copper Steel*. *Jour. Ind. and Eng. Chem.*, March, 1916.

the form of black sheets of 26 gauge:

1. Bessemer Steel.
2. Open Hearth Steel.
3. Charcoal Iron.
4. Commercially Pure Iron.
5. Commercially Pure Iron.
6. Copper-Bearing Iron.
7. Copper-Bearing Steel.
8. Copper-Bearing Bessemer Steel.
9. Copper-Bearing Open-Hearth Steel

These materials analyzed as follows:

	Copper	Manganese	Carbon	Phosphorus	Sulphur	Silicon
1	Trace	0.300	0.01	0.087	0.054
2	Trace	0.413	0.01	0.079	0.041
3	0.044	0.031	0.01	0.050	0.024	0.020
4	0.016	0.028	0.01	0.009	0.025
5	0.028	0.009	0.01	0.006	0.024
6	0.237	0.006	0.01	0.004	0.054
7	0.181	0.100	0.01	0.003	0.027
8	0.256	0.315	0.08	0.092	0.046
9	0.268	0.387	0.01	0.052	0.024

Before starting a work of this character, which involved quite some labor, due consideration was given to the methods of testing and in particular to those methods about which there is some difference of opinion. Questions arose concerning the desirability of a previous heat treatment and the necessity and means of removing mill-scale previous to testing.

Opinions differ as to whether samples of iron should be tested just as received or whether all test-pieces should receive some treatment so that the physical properties will be as nearly identical as possible. One author contends that samples should be tested as purchased, since the material that the samples represent will be used just as purchased. On the other hand, there are those who contend that all samples tested should have as nearly the same treatment as possible, in order to eliminate as many of the variables as possible. They suggest, therefore, that the test-pieces be annealed at the same temperature and that mill-scale be removed.

It would seem that the method used for testing should depend upon the use to which the data is to be put. If

the results are intended for the ultimate consumer the material should be tested just as purchased since this is the condition that it is used by the ultimate consumer. On the other hand, if the data is for scientific purposes such as determining the effects of various elements in the material, all variables other than the ones under investigation should be removed if it is possible to do so.

However, to make the work as broad and as complete as possible, it was decided not to limit the test to one method, but to try out both ways and to determine the relationship between the two.

Since part of the specimens were to have the mill-scale removed, the question arose as to what method should be used for removing this scale. In previous published work, very little has been said about the method of cleaning test specimens. When stated, however, it has usually been done by mechanical means such as filing or grinding, or by chemical means such as acids. Experiments were, therefore, conducted on the effects of methods of removing mill-scale upon the subsequent corrosion. The results of these experiments have already been published.⁷ It was shown in this paper that methods of cleaning by the use of chemicals had a profound effect upon the rate of corrosion, especially on tests of short duration.

In the contemplated test a clean iron surface was necessary in which the surface iron was in the same physical and chemical state as the iron beneath the surface. It was, therefore, decided that removal of the mill-scale by pickling in sulphuric acid, thorough washing with water and drying and subsequent removal of the surface iron with fine emery cloth would give a surface that was identical with the material itself.

The question also arose as to the method by which corrosion was to be estimated. There is a choice of methods to determine the rate of corrosion. One method commonly used is to determine

⁷ Richardson, E. A. The Effect of Pickling on the Corrosion of Iron. Met. and Chem. Eng., 12, 759.

the loss in weight after exposure for a given length of time and considering this loss as an index of corrosion. Another method is to allow the test specimens to corrode until failure occurs and to take the length of time as an index of corrosion. Inasmuch as there is some question as to the reliability of the "loss in weight" method, it was thought best to continue the test to the failure of the specimens.

This made it necessary to decide upon some standard condition at which failure could be considered to have taken place. Evidently, failure should not be taken at a point when the iron has completely rusted away or even when it has

method, it is believed that the life of each material was obtained to within an error of three or four weeks.

The sheets of 26-gauge iron were accordingly prepared for test by cutting into pieces 5 in. x 8 in. (12.7 cm. x 20.3 cm.). For the test on the material as received ten pieces of each kind of iron, that were found by measurement to be of standard thickness, were used. For the test on the prepared material, a number of pieces of each material were annealed at a red heat and then cleaned by the method already described. Great care was taken to give all of these test pieces exactly the same treatment. Ten of the prepared specimens of each ma-



Fig. 1

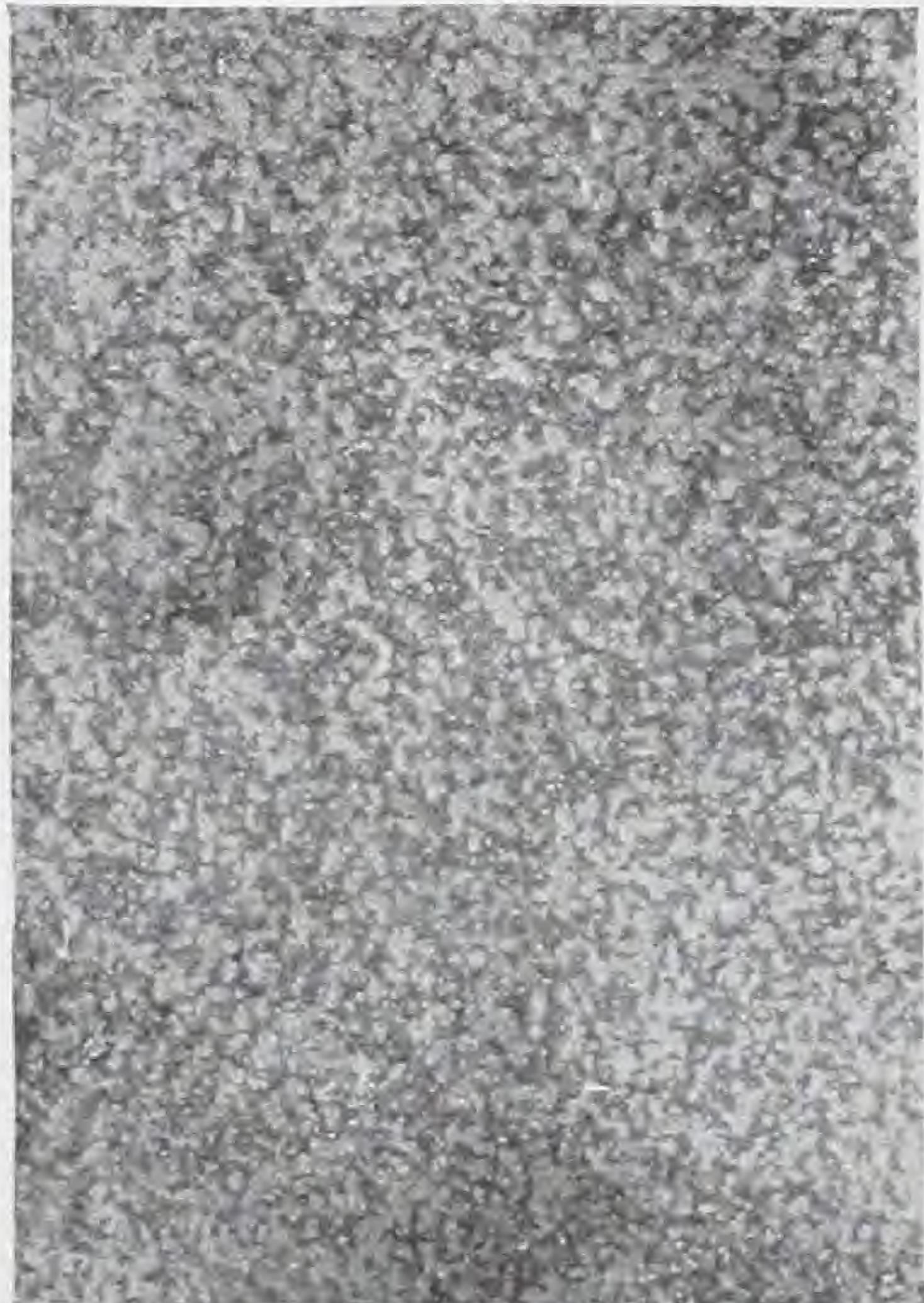


Fig. 2

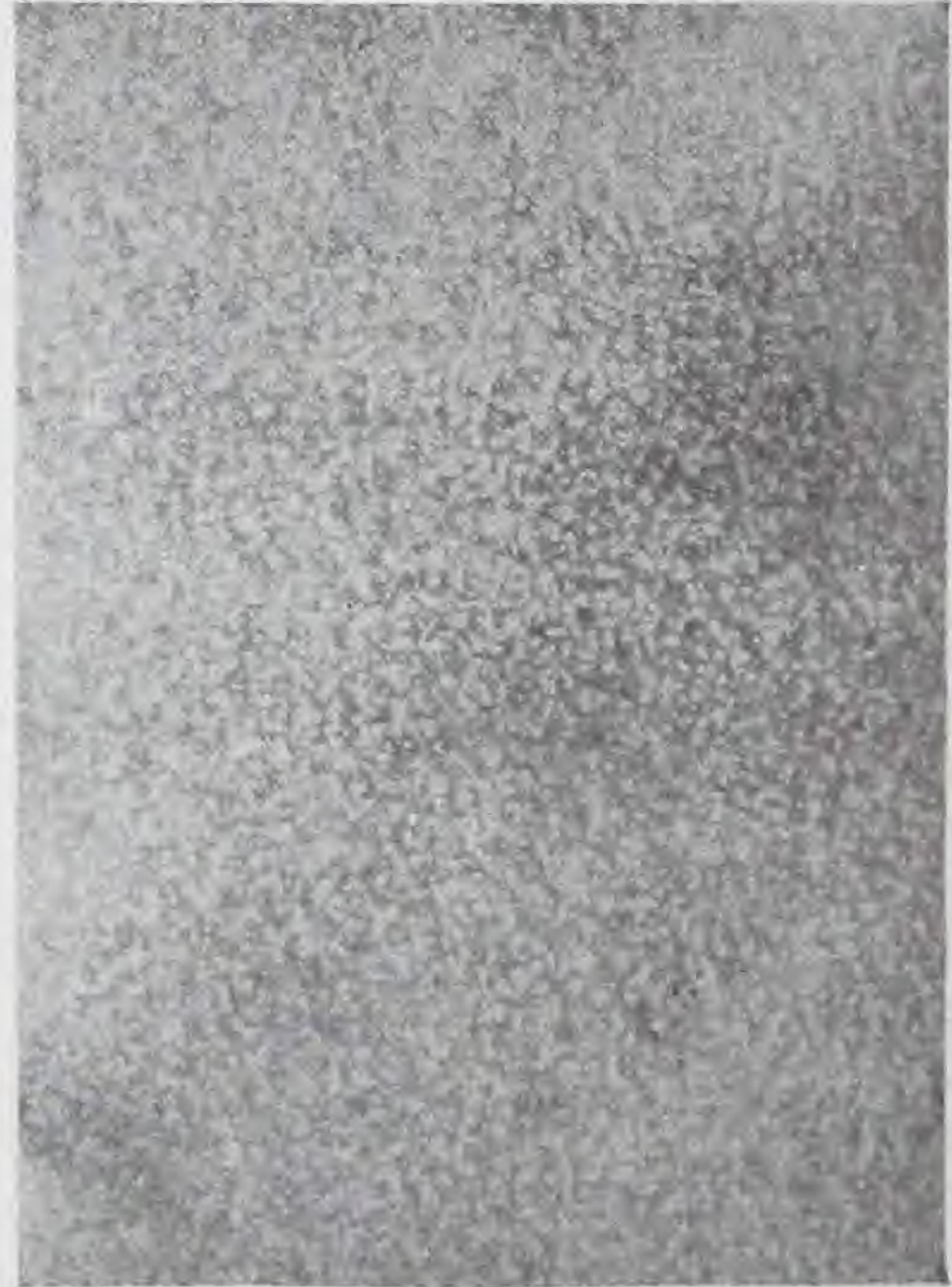


Fig. 3

almost disintegrated, since any sheet iron in service would be of no value long before such a condition obtained. The point of failure selected was when the sheet iron was in such a condition that it could be seen to be perforated when the rust was removed by gentle tapping with a blunt object such as a file or nail. By using one specimen of each kind of material as a test piece that was tapped and examined at intervals of about two weeks, a close approximation to the time of failure could be obtained. Thus the other specimens were not molested until the latter part of their useful life and the effects of tapping were practically eliminated from the results. By this

material that were found by measurement to be of the same thickness were taken for test. These prepared pieces were of practically the same thickness as the "as received" samples tested, due, no doubt, to the extreme thinness of the mill-scale.

On account of the precautions taken as regards uniform thickness of materials, the method of estimating failure and the method of cleaning surface, it is believed that the test should be comparative.

All samples were then placed securely in a wooden rack and exposed to the weather May 24, 1914. The atmosphere was what might be described as a semi-country one, and cannot be taken as an atmospheric acid test.

At the very start a marked difference was noted in the character of the rust formed on different materials. Whereas, on the Bessemer and open-hearth steel samples, the rust was of a yellowish-red color and became loose rapidly, the rust on the others was dark red in color and much more adherent. This adherent state seemed to reach its maximum in the copper steels, where the rust was very dark and fine grained. Fig. 1, Fig. 2 and Fig. 3 represent photographs taken about one year after the test was started and conveys in a rather poor way the character of the rust. Fig. 1 is characteristic of Bessemer and open-hearth steel. Fig. 2 is characteristic of charcoal iron, of commercially pure iron and iron containing copper, and Fig. 3 is characteristic of copper-bearing steels.

From visual observations at this time there appeared to be little difference between pure irons with or without additions of copper.

The life of the different materials tested is given below; each figure being an average of ten test pieces and represents the time for failure in days:

Material as Received	Material Annealed and Surface Cleaned
1 348	363
2 367	381
3 615	558
4 598	437
5 675	467
6 743	601
7 } 8 } 9 } 1200 (estimated)	1200 (estimated)

At the present writing the three samples of copper-bearing steel are still in good condition. The rust is still adherent and the underlying metal is still intact. The life of these steels have been estimated at 1200 days, which figure the writers believe is very conservative. These specimens are still exposed to the weather and will be until failure occurs.

Conclusions. Taken as a whole, the results indicate that copper-bearing steels are, without doubt, decidedly superior to any of the other materials

tested. The remaining materials may be divided roughly into two classes, one class including the ordinary steels (Bessemer and open-hearth) and the other class, the commercially pure irons and the copper-bearing irons. Charcoal iron is classed with the pure irons. We have obtained results in another test which would indicate that the resistance of wrought iron to corrosion is due to the purity of its iron and not to slag inclusions. In addition, it was noted during the present test that charcoal iron appeared to corrode in very much the same way as pure iron.

In regard to the steel-iron question it is noted that the pure irons (including charcoal iron) are superior to steel. It is believed that this superiority is due to the purity of the iron, or to some combined effect of manganese and copper.

The results obtained in regard to the effects of mill-scale do not agree with the results obtained by others. They indicate that with steels which rust rapidly, mill-scale is a stimulator of corrosion. On the other materials tested, the mill-scale has exerted a protective action. We have no explanation for this.

The important feature of the results, however, is that it substantiates the claim made in several other publications that the addition of copper to steel in amounts of about 0.25 percent causes a remarkable increase in its ability to resist atmospheric corrosion. In the present test, the addition of about 0.25 percent copper to Bessemer or open-hearth steel has resulted in an increased resistance of 300 or 400 percent.

The addition of copper to pure iron also results in an increased resistance to corrosion, but to no such an extent as the addition of a similar amount to steel. The addition of about 0.25 percent copper to a commercially pure iron results in the useful life being increased by about 20 percent. This figure was arrived at by comparing the average life of irons Nos. 3, 4 and 5 with No. 6.

We have been unable to determine the reason for this effect of copper in reducing corrosion. It is believed, in view of the fact that the copper exerts a greater influence in steel than in iron, that it must be due to the combined presence of copper and manganese, since the chief difference in the iron and steels under consideration is in the manganese content. It may be that the copper eliminates a harmful effect of manganese, or it may be that it is some combined effect of these two elements that acts as a protection to iron. The writers are inclined to believe that it is the latter cause.

This conclusion, the writers believe, is also confirmed by the results of other observers. Mr. D. M. Buck⁸ tested several kinds of sheet irons and steel by exposing pieces 2 in. x 4 in. (5.08 cm. x 10.16 cm.), 27 gauge, to the atmosphere in a mill yard at McKeesport, Pa., and found the loss in weight after eleven months to be as noted in table below.

Similar results were obtained upon tests made at Scottdale, Pa., and in McKeesport city water. These tests indi-

⁸ Buck, D. M. Recent Progress in Corrosion Resistance. Amer. Iron and Steel Inst., May, 1915.
Also pamphlet. Keystone Copper-Bearing Steel. American Sheet and Tin Plate Co.

cate that copper even up to 0.10 percent added to low manganese materials increases their resistance to corrosion but little. Ordinary steels containing about 0.40 percent manganese, but no copper, are very poor as regards resistance to corrosion but additions of copper to such steels result in a greatly increased resistance. A maximum resistance is reached with about 0.25 percent copper. These results were also confirmed upon full-sized sheets of the same materials and in the above cited papers several excellent photographs are given.

The writers believe, in view of these results, that the resistance of pure iron to corrosion could be increased by the addition of both manganese and copper and that additions of manganese to pure iron or steel, even up to 3 or 4 percent, or more, with a corresponding increase in copper to produce a maximum effect should give a material more resistant to atmospheric corrosion than the copper steel now on the market.

Also, some interesting results might be obtained by substituting for manganese in copper-bearing steels or irons, chromium, vanadium, tungsten, or molybdenum.

TABLE

No.	C.	Mn.	S.	P.	Si.	Cu.	Loss*	Condition of Test-Pieces After Exposure
E	.04	.30	.043	.06531	2.65	No holes.
V	.04	.39	.078	.11431	2.75	No holes.
Z	.04	.43	.049	.099	.011	.25	2.83	No holes.
D	.06	.50	.037	.01626	2.94	No holes.
C	.06	.33	.035	.01825	2.96	No holes.
H	.042	.16	.024	.00321	3.05	Few holes in 2 pieces.
O	.027	.07	.033	.00709	3.31	Few holes in 4 pieces.
W	.049	.05	.043	.00510	3.72	Many holes in all pieces.
J	.022	.03	.031	.006034	4.17	Many holes in all pieces.
I	.03	.06	.013	.052	.039	.07	4.26	Many holes in all pieces.
Y	.04	.45	.046	.099	.006	Trace	6.94	Only a lace work of steel left.

* Loss given in oz. per sq. ft.

Summary

- 1.—Copper-bearing steels are decidedly superior to pure iron, steel, or charcoal iron.
- 2.—The addition of copper to pure iron increases its resistance to corrosion, but to no such an extent as similar additions to steel.
- 3.—Charcoal iron and pure iron are superior to steel as regards resistance to atmospheric corrosion.
- 4.—Charcoal iron is very similar to pure iron in its resistance to corrosion.
- 5.—Copper is believed to decrease corrosion due to some mutual influence of manganese and copper.
- 6.—The additions of larger amounts of manganese and copper to pure iron or steel are suggested as well as additions of copper-chromium, copper-vanadium, copper-tungsten, or copper-molybdenum.
- 7.—Mill-scale stimulates corrosion in rapidly rusting materials and retards it in slowly rusting materials.

*The American Sheet and Tin
Plate Company, Pittsburgh,
Pa., will, upon request, fur-
nish to all interested, copies
of the paper by Messrs. D.
M. Buck and J. O. Handy,
entitled "Research on the
Corrosion Resistance of Cop-
per Steel," mentioned on
page three of this paper.*



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